

REMARKS

Claims 1-9, 12, 13, and 15-29, as amended, remain herein. Claims 17-23 are currently withdrawn. Claims 10, 11 and 14 have been cancelled without prejudice. New claims 28-29 have been added. Support for the new claims may be found throughout the specification (see, e.g., original claims).

1. Claims 1, 5-9, 13, 15, 16 and 24-27 were rejected under 35 U.S.C. § 102(b) over Kioka et al. U.S. Patent 5,055,528. The Office Action states that Kioka's Example 1 discloses applicants' method of producing the alkoxy-containing compound.

Applicants' claims 1 and 9 recite a solid catalyst component obtained by reacting certain compounds including an alkoxy-containing magnesium compound obtained by reacting metal magnesium, an alcohol and a halogen and/or a halogen-containing compound containing at least 0.0001 gram atom of halogen atoms per mol of the metal magnesium.

Kioka discloses the use of alkoxy magnesium halides (see Kioka at col. 6, lines 23-26); however, Kioka does not disclose an alkoxy-containing magnesium compound that is obtained by reacting metal magnesium, an alcohol and a halogen and/or a halogen-containing compound containing at least 0.0001 gram atom of halogen atoms per mol of the metal magnesium. The use of the claimed alkoxy-containing magnesium compound achieves a high catalyst activity and a polymer with excellent powder morphology as evidenced in the Declaration of Shojiro Tanase submitted on November 5, 2007.

In addition, contrary to the assertion in the Office Action, the process of Kioka's Example 1 does not yield an alkoxy-containing magnesium compound but a compound having

the formula  $MgCl_2(C_8H_{17}OH)_x$  (see enclosed article: Di Noto et al., "MgCl<sub>2</sub>-supported Ziegler-Natta catalysts: A structural investigation by X-ray diffraction and Fourier-transform IR spectroscopy on the chemical activation process through MgCl<sub>2</sub>-ethanol adducts," *Die Makromolekulare Chemie* 2003, 193(7), 1653-1663). Furthermore, the process of Kioka's Example 1 is also described in applicants' Comparative Example 1 and results in inferior catalyst activity and polymer powder morphology (see Table 1 at page 58 of applicants' specification).

Thus, Kioka does not disclose all limitations of applicants' claims and, therefore, it is not a proper basis for a rejection under § 102(b). Applicants respectfully request reconsideration and withdrawal of this rejection.

2. Claims 1-9, 12-13, 15 and 16 were rejected under 35 U.S.C. § 103(a) over Kioka in view of Yukimasa et al. U.S. Patent 6,423,782.

Applicants' claims 1 and 9 recite a solid catalyst component obtained by reacting certain compounds including an alkoxy-containing magnesium compound obtained by reacting metal magnesium, an alcohol and a halogen and/or a halogen-containing compound containing at least 0.0001 gram atom of halogen atoms per mol of the metal magnesium.

As discussed above, Kioka does not disclose an alkoxy-containing magnesium compound that is obtained by reacting metal magnesium, an alcohol and a halogen and/or a halogen-containing compound containing at least 0.0001 gram atom of halogen atoms per mol of the metal magnesium. Yukimasa does not teach what is missing from Kioka. Specifically, Yukimasa does not teach or suggest the amount of halogen used when preparing the alkoxy-containing magnesium compound. As discussed above, the use of the claimed alkoxy-containing

Serial No. : 10/542,753  
Attorney's Docket No.: 28955.1053

magnesium compound achieves a high catalyst activity and a polymer with excellent powder morphology as evidenced in the Declaration of Shojiro Tanase submitted on November 5, 2007.

Thus, none of Kioka, Yukimasa, or anything else in this record discloses or suggests applicants' claims. In addition, there is no disclosure or suggestion in any of Kioka, Yukimasa, or anything else in this record that would have suggested the desirability of combining any portions thereof effectively to anticipate or render obvious applicants' claimed invention. Thus, reconsideration and withdrawal of this rejection are respectfully requested.

For the foregoing reasons, all claims 1-9, 12, 13, 15, 16 and 24-29 are now fully in condition for allowance, which is respectfully requested. The PTO is hereby authorized to charge or credit any necessary fees to Deposit Account No. 19-4293. Should the Examiner deem that any further amendments would be desirable in placing this application in even better condition for issue, he is invited to telephone applicants' undersigned representative.

Respectfully submitted,

Date: September 23, 2008

Houda MORAD  
Roger W. Parkhurst  
Registration No. 25,177  
Houda Morad  
Registration No. 56,742

STEPTOE & JOHNSON LLP  
1330 Connecticut Avenue NW  
Washington DC 20036-1795  
Tel: (202) 429-6420  
Fax: (202) 429-3902



## MgCl<sub>2</sub>-supported Ziegler-Natta catalysts: a structural investigation by X-ray diffraction and Fourier-transform IR spectroscopy on the chemical activation process through MgCl<sub>2</sub>-ethanol adducts

Vito Di Noto, Roberto Zanetti\*, Maria Viviani, Carlo Marzola, Antonio Mariga, Silvano Bresadola

Dipartimento di Chimica Inorganica, Metalloorganica ed Analitica dell'Università, via Loredan 4, I-35131 Padova, Italy

(Date of receipt: September 24, 1991)

### SUMMARY:

By X-ray diffraction on polycrystalline powders and Fourier-transform IR spectroscopy, some adducts  $MgCl_2(C_2H_5OH)_x$  were studied, having different composition in the range from  $x = 0$  ( $\alpha$ -MgCl<sub>2</sub>) to  $x = 6$ . For  $2 < x \leq 6$ , the structure of such adducts shows prevalently ionic Mg—Cl bonds. For  $x \leq 2$ , covalent bonds are observed among chlorine and magnesium atoms, which give rise to chain compounds through chlorine bridges among the Mg-atoms. The obtained structural data are also discussed in terms of the synthesis of some MgCl<sub>2</sub>-based supports which are very active in the Ziegler-Natta process of olefin polymerization, after a treatment with titanium halides and a successive addition of a cocatalyst and of other suitable donors.

### Introduction

The chemical interactions among MgCl<sub>2</sub> and some electron-donor compounds B (or Lewis bases) are at the present time the subject of several investigations, concerning both the structural characterization of the  $MgCl_2 \cdot nB$  adducts, which are obtained by synthesis of MgCl<sub>2</sub> and B<sup>1-3</sup>, and their use as supports for compounds (especially halides) of titanium in the preparation of industrial Ziegler-Natta catalytic systems for olefin polymerization processes<sup>1,3</sup>. The physical and chemical characterization of such systems is therefore justified also in terms of some industrial applications: as a matter of fact, at first the study of some basic crystallographic properties, and especially of the disorder and polymorphism phenomena<sup>4-7</sup> in MgCl<sub>2</sub>, and successively the investigation of MgCl<sub>2</sub>·nB compounds, which after thermal treatment provide very active supports based on MgCl<sub>2</sub>, demonstrated the usefulness of joining to the preparative methods a careful characterization of all these compounds, including the intermediate ones.

The treatment of  $\alpha$ -MgCl<sub>2</sub> with a Lewis base B produces some well defined adducts, and a successive and suitable elimination of B from these adducts gives rise to a solid support, whose crystal structure is disordered and which results in the practice very active in the polymerization catalysis. Such a procedure represents one of the modern methods for the industrial preparation of active supports, and it is often indicated, in the scientific and patent literature, by the term *chemical activation*.

In some previous investigations<sup>8</sup>, we demonstrated that all the adducts having MgCl<sub>2</sub>·nB composition show a similar chain structure, as clearly indicated by X-ray



diffraction (XRD) methods on both polycrystalline powders and especially single crystals; the repeating units are linked through chlorine bridges among the Mg atoms. Since the successive physical and chemical characterization of the above adducts shows some interesting relationships, which are valid in the whole group of adducts, we describe in the present paper some details of our work, related to the study of adducts  $MgCl_2(C_2H_5OH)_x$ , in the range  $0 < x \leq 6$ , also compared to the structure of  $MgCl_2$  in its different forms<sup>9</sup>. In this investigation we employed X-ray diffraction, Fourier-transform IR and thermal techniques, but a particular relevance is assigned here to the first two methods, since they supply some particular information related to the structural aspects of the examined compounds.

#### Experimental part

##### Reagents

Anhydrous  $\alpha$ - $MgCl_2$  was provided by Himont Italia S.p.A. Ferrara, Italy. Ethanol, an ACS reagent, was further purified and dehydrated by standard methods.

##### Instrumentation

The thermogravimetric (TG) analysis of the adducts was performed by a TGS-2 Perkin-Elmer thermobalance, operating in a strictly inert ( $N_2$ ) atmosphere inside a Braus MB-150 L/U dry-box. The TG patterns were collected under a working dynamic flux of  $N_2$  of  $50 \text{ cm}^3 \cdot \text{min}^{-1}$  at a heating rate of  $20^\circ\text{C min}^{-1}$ .

The Fourier-transform IR (FT-IR) spectra in the medium (MIR) and far (FIR) infrared were collected by a Nicolet 3DXC spectrophotometer, equipped with a triglycine sulfate (TGS) detector at a nominal resolution of  $4 \text{ cm}^{-1}$  and collecting 200 scans; the Happ-Genzel apodization method<sup>10</sup> was adopted.

The MIR spectra were recorded after suitable dispersion of the samples in anhydrous KBr pellets and transferring the pellets into a sealed cell equipped with KBr windows. The FIR spectra were collected after suspension of the samples in *cujol*, transferring the suspension into a sealed cell provided with polyethylene windows. The X-ray diffractions (XRD) patterns were scanned in the transmission technique, using a GID-2000 diffractometer produced by Ital Structures (Riva del Garda, Italy), operating in the Seemann-Bohlin geometry and equipped with a quartz curved-crystal monochromator of the Johann type aligned on the primary beam. The  $Co-K\alpha$  radiation ( $\lambda = 1.3406 \text{ \AA}$ ) was employed, and an instrumental  $2\theta$  step of  $0.1^\circ$  every 10 s was selected.

The samples for XRD measurements were prepared in a dry-box and maintained in a strictly inert  $N_2$  atmosphere for all the time of measurement.

##### Synthesis of the adducts $MgCl_2(C_2H_5OH)_x$

The adduct having the composition  $MgCl_2(C_2H_5OH)_x$  was prepared<sup>10,11</sup> by treating 3 g of  $\alpha$ - $MgCl_2$  under reflux for 2 h with  $100 \text{ cm}^3$  of  $C_2H_5OH$ , in a strictly inert atmosphere, with stirring and at the b. p. of the mixture. The obtained solution, after a slow cooling overnight and in the dark, separated some needle-shaped, transparent and highly unstable crystals. After washing and drying three times with  $10 \text{ cm}^3$  of heptane, these crystals gave a white, polycrystalline solid. By gradual slow elimination of  $C_2H_5OH$  from this solid at  $50^\circ\text{C}$  and 0.1 atm, the group of adducts was obtained having different compositions  $MgCl_2(C_2H_5OH)_x$  in the  $0 < x \leq 6$  range.

Fig. 1 shows the variation of the mole ratio  $C_2H_5OH/MgCl_2$  as a function of the  $C_2H_5OH$  content, determined by TG analysis in the above samples. Some of these analytical data were also confirmed by FT-IR-ATR (attenuated total reflectance) spectrometry<sup>9</sup>.

## MgCl<sub>2</sub>-supported Ziegler-Natta catalysts: Synthesis and X-ray diffraction characterization of some MgCl<sub>2</sub>-Lewis base adducts

Vito Di Nata, Antonio Mariga, Maria Viviani, Carla Marega, Silvano Bresadola,  
Roberto Zanetti\*

Dipartimento di Chimica Inorganica, Metalorganica ed Analitica dell'Università,  
Via Loredan, 4 - I-35131 Padova, Italy

(Date of receipt: April 15, 1991)

### SUMMARY:

Some adducts of MgCl<sub>2</sub> and Lewis bases (or donors) B were examined, having a composition MgCl<sub>2</sub> · 2B, where B = Ethyl (Et) formate, Et acetate, Et propionate, Et benzoate, Et crotonate, acetone, 2-butanone and EtOH. The crystallographic investigation of these adducts, carried out on polycrystalline powders and some single crystals, shows some remarkable structural analogies for all examined donors. In particular, the X-ray diffraction patterns of the adducts indicate the total absence of the close-packing of chlorine which characterizes α-MgCl<sub>2</sub> and the presence of covalent Cl-Mg-Cl chains. The obtained data are correlated with the preparation of active supports for Ziegler-Natta olefin polymerization: after total elimination of B, a disordered structure of MgCl<sub>2</sub> is obtained, which is coincident with the reported one for the mechanically activated (by ball-milling) MgCl<sub>2</sub> and previously described both in the scientific and in the patent literature.

### Introduction

The investigation of some particular interactions among MgCl<sub>2</sub> and Lewis bases (or donors) presents an increasing interest in studies on heterogeneous Ziegler-Natta catalysis for olefin polymerization. Actually, systems based on MgCl<sub>2</sub>, a titanium halide, one (or two) electron donors and a cocatalyst containing Al-alkyls represent modern and very active catalysts in the above polymerization processes<sup>1,2</sup>. These investigations are also important in obtaining significant improvements in the catalyst performances, with respect to both the carrier (or support) preparation, generally based on polycrystalline MgCl<sub>2</sub>, showing a peculiar morphology<sup>3,4</sup> and the influence of a successive addition of especially designed donors to improve the stereoregularity of the obtained polymers. Some physico-chemical methods, and in particular the techniques for structure determination, can in practice contribute to these studies, but we consider the X-ray diffraction (XRD) methods, and in general the diffractometric ones, eventually associated with nuclear magnetic resonance (NMR)<sup>5</sup> and Fourier transform infrared (FT-IR)<sup>6</sup> measurements, giving the best information both for research and for the support control. This statement is essentially based on XRD investigations on single crystals and polycrystalline powders of adducts which are strictly connected with the supports.

The donors B used in the present study include some esters, ketones and ethanol. Considering the strong analogies observed in the series of MgCl<sub>2</sub>-donor examined compounds, we report in the present paper some details on their preparation and